Genesis and Behaviour of Ultramafic Soils and Consequences for Nickel Biogeochemistry

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Abstract

Ultramafic outcrops could represent up to 3% or more of the terrestrial surface and their unusual geochemistry makes them a global hotspot for biodiversity. Ultramafic soils are a peculiarity for soil scientists in all climatic zones of the world. These soils lack essential pedogenetic elements including Al, Ca, K and P. Whereas serpentinites will most likely give birth to Eutric Cambisols with little influence by climate, peridotites will induce an acceleration of weathering processes; this over-expressed weathering is due to their deficiency in Si and Al, abundance in Mg, and lack of secondary clay formation. Soils evolve towards Ferralsols in tropical conditions. Results from isotopic dilution techniques show that Ni borne by primary minerals is unavailable. Secondary 2:1 clay minerals (e.g. Fe-rich smectite) and amorphous Fe-oxyhydroxides are the most important phases that contain available Ni. Therefore, smectite-rich soils developed on serpentinite and poorly weathered Cambisols on peridotite (only in temperate climates) are the soils with highest Ni availability. Although soil pH conditions are a major factor in controlling available Ni, the chemical bounds of Ni to bearing phases are even more important to consider. Plants may take up significant amounts of Ni, and its biogeochemical recycling seems an essential factor that explains Ni availability in the surface horizons of ultramafic soils.

1 Introduction

Globally, ultramafic (or ultrabasic) outcrops represent more than 3% of the terrestrial surface, according to a recent estimation (Guillot and Hattori 2013). They have focused attention for decades because of their unusual geochemical composition at the surface of continents. This peculiar geochemistry (lack of most essential elements for plant nutrition: K, Ca and P) makes them a global hotspot for biodiversity. To soil scientists (Alexander 2009), ultramafic soils have also been of a particular interest because the pedogenetic processes involved in their formation are usually different from those taking place in soils developed on all other types of bedrock in the same area. It is quite common that ultramafic soils in warm regions display soil types that are

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common in colder regions, or the opposite. Ultramafic soils are also the most important source of Ni and Co to terrestrial ecosystems (Estrade et al. 2015). Nickel and Co hyperaccumulation by plants has evolved a great deal from ultramafic soils, mostly in relation to metal bioavailability within these soils (Lange et al. 2017; van der Ent et al. 2016a, 2018a). This chapter discusses the most important trends of soil genesis and evolution on ultramafic bedrock worldwide. It then focuses on the main Ni-bearing phases resulting from soil genesis patterns in the most important cases, providing a foundation for a better understanding of the factors that control Ni availability in ultramafic soils.

2 Properties of Ultramafic Bedrock

2.1 What Are Ophiolites and Peridotites?

Ophiolites, which were long regarded as continental analogs of oceanic crust, are now viewed as out-of-place fragments of oceanic lithosphere (Dilek and Furnes 2009). They generally consist of some or all of the following components: lherzolite or harzburgite commonly altered to serpentinite, gabbro, 'sheeted' basic dykes, pillow-bearing basic volcanic rocks, chert, and sedimentary rocks (Vaughan and Scarrow 2003). Ultramafic outcrops occupy 1–3% of Earth's land surface (Fig. 1) but are locally abundant in ophiolite belts along tectonic plate margins (Coleman and Jove 1992; Vaughan and Scarrow 2003; Dilek and Furnes 2009, Guillot and Hattori 2013). One of the most studied ophiolite complexes is that of the ancient Tethyan Ocean, which spread from the Alps to the Himalayas, and was subducted onto the margin of the continental Eurasian plate from Jurassic to Cretaceous time (Dilek and Furnes 2009). Ophiolites worldwide, including upper mantle peridotites, vary in lithology and geochemistry owing to differences in compositions of magmas over time and according to regional conditions (Dilek and Furnes 2009).

2.2 Varieties of Ultramafic Rocks and Their Compositions

Peridotite (or ultramafic) rocks are defined as igneous rocks that contain more than 90 vol% mafic minerals (Le Bas and Streckeisen 1991), of which are olivine (nesosilicates), and pyroxene (inosilicates). There are several types of peridotites based on vertical position in the original ophiolite, being distinguished according to the ratio of olivine to clino- and ortho-pyroxene (Fig. 2) as officially defined by the International Union of Geological Sciences, i.e. IUGS (Le Bas and Streckeisen 1991). The most common ultramafic rocks found in outcrops include dunite, harzburgite, lherzolite and pyroxenite.

All of these rocks can undergo metamorphism in varying conditions according to the history of mid-ocean ridges and subduction zones (O'Hanley 1996; McCollom et al. 2016). This process includes deformation—including shearing—and of course serpentinization (Fornasaro et al. 2019), which essentially consists of a hydration of olivine and pyroxene that results in the formation of serpentine clay minerals; however, other minerals are also typically formed during the serpentinization process, e.g. magnetite, brucite, talc, chlorite, etc. (Coleman and Jove 1992; McCollom et al. 2016). As an example, the formation of serpentine through the weathering of olivine is described in Eq. (1) (McCollom et al. 2016):

$$\underset{\text{Olivine(Forsterite)}}{Mg_{1.82}Fe_{0.18}SiO_4} + wH_2O \rightarrow 0.5\underset{\text{Serpentine}}{\left(Mg, Fe^{II}, Fe^{III}\right)_3\left(Si, Fe^{III}\right)_2O_5(OH)_4} + x\underset{\text{Brucite}}{(Mg, Fe)(OH)_2} + y\underset{\text{Magnetite}}{Fe_3O_4} + zH_2 \quad (1)$$

Serpentines are 1:1 clay minerals and comprise three different types: chrysotile (asbestos form—Fig. 3c), lizardite, and antigorite (platy form). Chrysotile is one of the most common serpentine-group minerals and typically displays long fibres due to self-winding of the clay-like

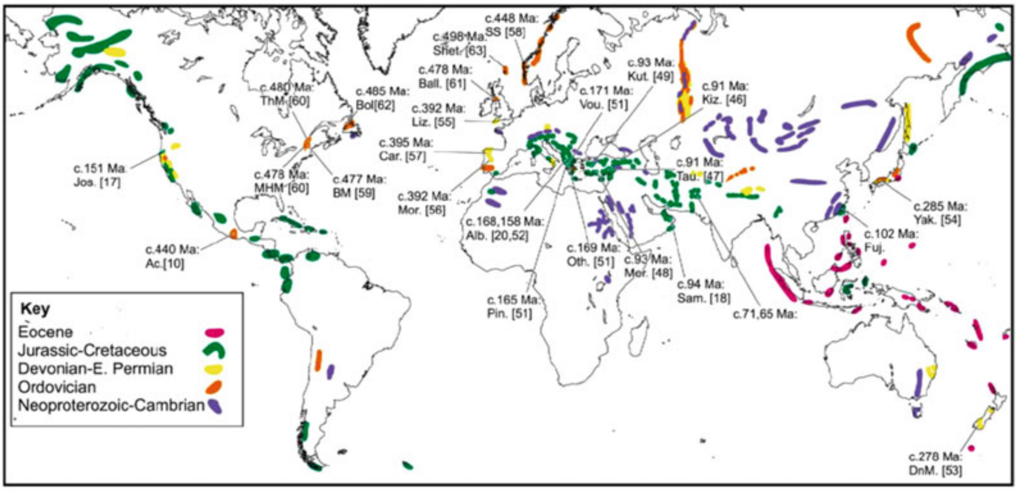

Fig. 1. Distribution of belts of Phanerozoic ophiolites cited in the text, including major Neoproterozoic and Phanerozoic occurrences. Note that ophiolites of several age pulses are represented in most belts. Scandinavian ophiolites [2]. Mediterranean and western Asia ophiolite distribution [3]. Central Asian ophiolites [4] apart from [5], western Pacific ophiolites [6], Uralian ophiolites [7], Alaskan ophiolites [8], western North American, Central American and Caribbean ophiolites [9] apart from [10,11], southern South American ophiolites [12,13]. Shet.: Shetland; Ball.: Ballantrae; ThM: Thetford Mines; MHM: Mont Ham Massif; BoI: Bay of Islands; BM: Boil Mountain; SS: Solund-Stavfjord; Car.: Careon; Ac.: Acatlán; Mor.: Morais; Liz.: Lizard; Yak.: Yakuno; DnM: Dun Mountain; Vou.: Vourinos; Oth.: Othris; Alb.: Albanian; Pin.: Pindos; Jos.: Josephine; Fuj.: Fujian; Sam.: Samail; Kut.: Kutahya; Mer.: Mersin; Tau.: Tauride; MB: Muslim-Bagh.

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Fig. 1 Distribution of ophiolite belts worldwide (from Vaughan and Scarrow 2003)

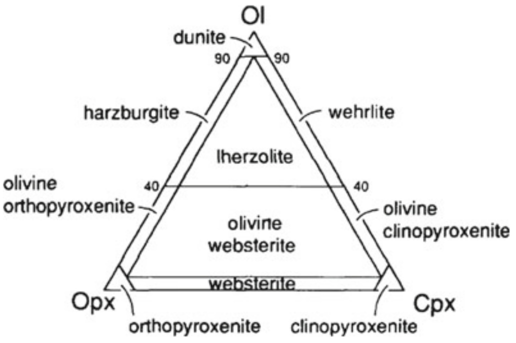

Fig. 2 Classification and nomenclature of the ultramafic rocks (mafic minerals >90%) based on the modal proportions of olivine (Ol), orthopyroxene (Opx) and clinopyroxene (Cpx) (from Le Bas and Streckeisen 1991)

sheets (Fig. 3). Where serpentinization results in the transformation of most olivine and pyroxene contained in the peridotite, then the rock is classified as serpentinite (O'Hanley 1996). The difference between peridotite and serpentinite is clear: the former is dark black with an oxidized weathering sheath (Fig. 3a), mainly due to Fe-oxide precipitation, whereas the serpentinite has a greener and uneven aspect (Fig. 3b) owing to particles of serpentine, talc, and other clay minerals, which produces a texture that resembles snake skin and gives the rock its name 'serpentine'. Because of its specific effect on the mineralogy, the serpentinization process is a key phenomenon in explaining the distribution of Ni and Cr among secondary mineral phases formed during the initial stages of rock weathering before complete pedogenesis (Fornasaro et al. 2019).

Secondary geological materials originally derived from ultramafic rocks such as mountain rock slides (Gasser et al. 1995; d'Amico et al. 2008), colluvium (Lee et al. 2004), sedimentary rocks (e.g. conglomerate, Fig. 4), and river alluvia (Estrade et al. 2015; Rinklebe et al. 2016), can also contribute to ultramafic soils and landscapes. Usually, these materials are not identified as ultramafic rocks on geological maps but are mentioned using different qualifiers based on geomorphological origin and period of deposition (e.g. glacial/fluvial deposits). According to the composition of the original minerals forming peridotites, ultramafic rocks have very high Mg (18–24 wt%) and high Fe (6–9 wt%), but very

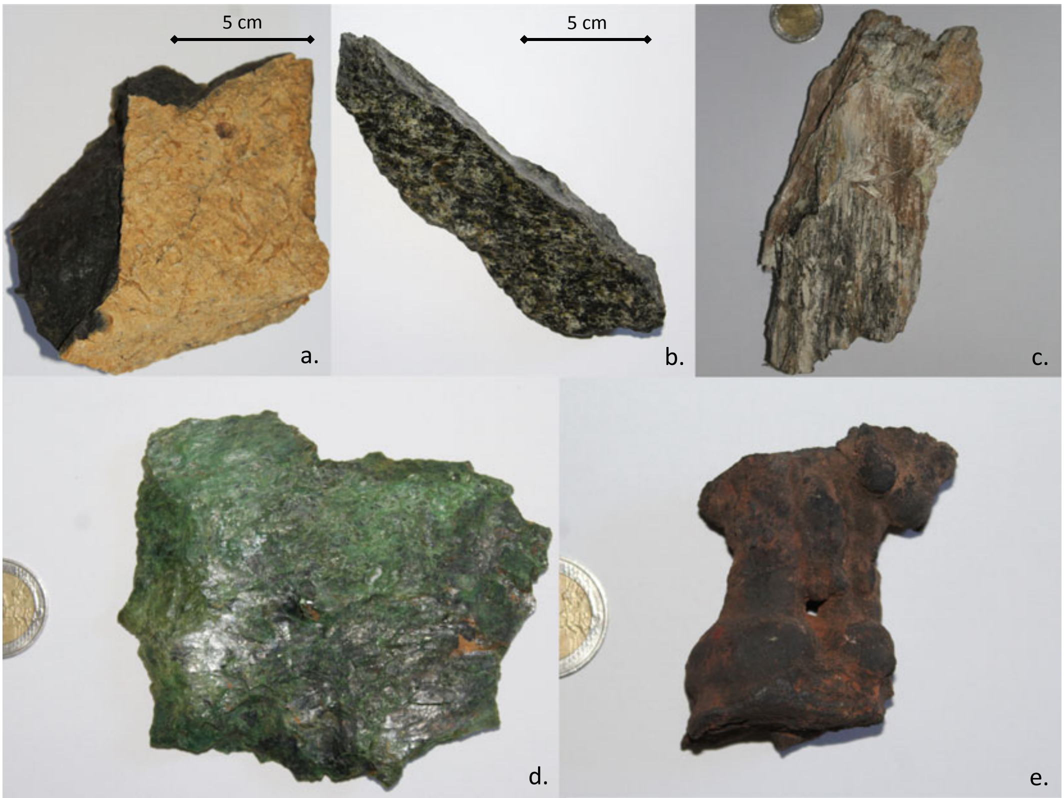

Fig. 3 **a** Olivine-rich peridotite with weathered surface from Shebenik (Albania). **b** Highly serpentinized peridotite from Pindus Mountains (Greece). **c** Large chrysotile fibres from the Barberton Greenstone belt (South Africa). **d** Garnierite: serpentine-like minerals with approx. 20% Ni (green colour) from the saprolite horizon of Geric Ferralsols in Vulcain Mine, La Tontouta (New Caledonia). **e** Fragment taken from the Petroplinthic horizon (ferricrete or iron pan) of a Geric Ferralsol in Yaté (New Caledonia) where two parallel earthworm galleries have been fossilised through Fe-oxide crystallization

low Ca (1–4 wt%) and Al (1–2 wt%) contents (Alexander 2004). The main weatherable minerals in peridotite and serpentinite (Lee et al. 2004; White and Buss 2014) are olivine, pyroxene, and clay minerals (mainly serpentine but also talc, chlorite, etc.).

3 Pedogenesis of Ultramafic Rocks and Soil Characteristics

The genesis, development, and functioning of soils developed on ultramafic materials have received a great deal of attention over the last 30 years. Firstly, ultramafic soils were studied due to their economic importance related to the genesis of nickeliferous laterites (Colin et al. 1990; Gleeson et al. 2003), but also because of their role in trace metal geochemistry (Becquer et al. 2006; Cheng et al. 2011; Bani et al. 2014; Kierczak et al. 2016). One of the major factors in influencing the genesis and characteristics of soils developed on ultramafics is the nature of the parent ultramafic rock (Alexander 2004, 2009; Alexander and DuShey 2011; Pędziwiatr et al. 2018; van der Ent et al. 2018a; Marescotti et al. 2019). Other major factors affecting soil genesis are climatic conditions, topographic situation (position in the toposequence), and vegetation cover (Bonifacio et al. 1997; Alexander and DuShey 2011; Chardot et al. 2007; Kierczak et al. 2007; Cheng et al. 2011; Bani et al. 2014; Hseu et al. 2018; van der Ent et al. 2018a). After compiling available descriptions on major

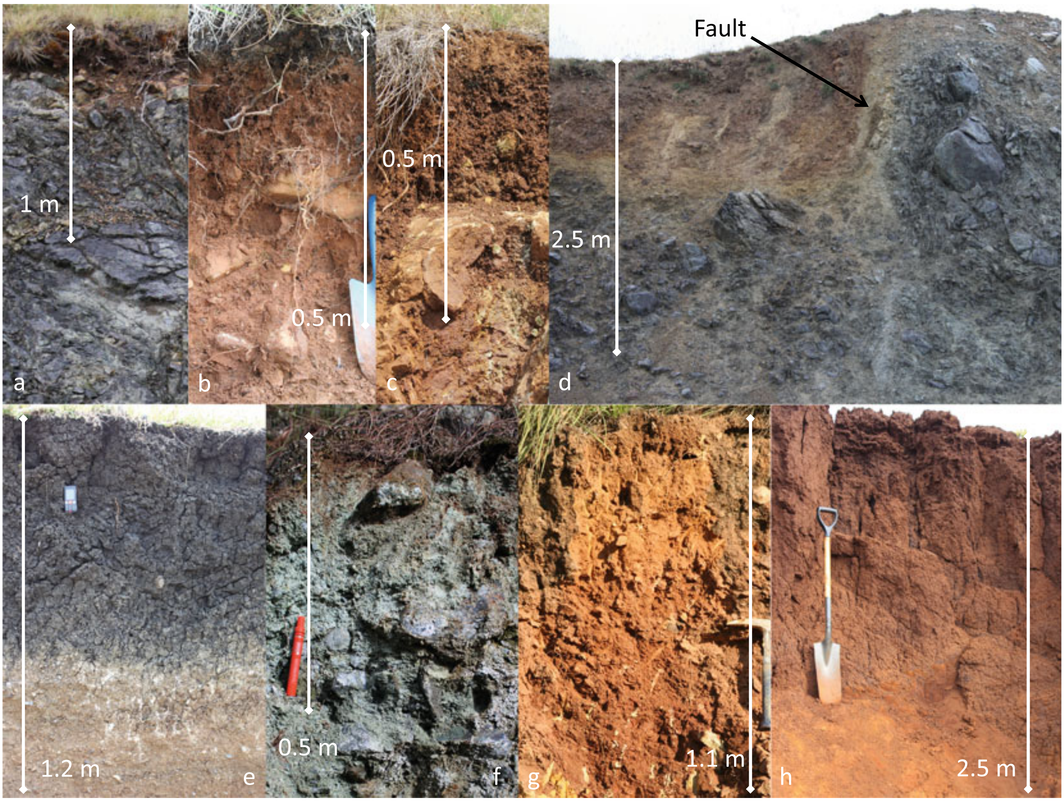

Fig. 4 Caracteristic pedons on ultramafic rocks globally: **a** Cambic Leptosol (Serpentinite 1700 m, Katara Pass, Greece). **b** Eutric Cambisol (Dunite, 1200 m, Qaftë Shtamë, Albania). **c** Chromic Cambisol (Dunite, 890 m, Trygona, Greece). **d** A fault between partially-serpentinized (left) and fully-serpentinized peridotite (right) (1700 m, Katara Pass, Greece). **e** Hypermagnesic Vertisol (Serpentinite, 650 m, Prrenjas, Albania). **f** Folic Leptosol (Serpentinite, 800 m, Kinabalu Park, Sabah, Malaysia). **g** Chromic Luvisol (Peridotite, 1100 m, Barberton, South Africa)—Geric Ferralsol (peridotite, 100 m, Goro, New Caledonia). Photographs: G. Echevarria

soils developed on serpentinite sensu stricto (Table 1), and on partially serpentinized peridotite (Table 2), it appears that most such soils reach a limited development stage, whatever the climatic conditions, which confers on them typical cambic and magnesic (exchangeable Ca/Mg < 1) properties with very few exceptions globally. These cambic properties are mainly derived from the formation of secondary clays of the 2:1 type—Fe-rich smectite and low-charge vermiculite—that form stable complexes in soils, typically with excess Mg ions (Bonifacio et al. 1997; Lee et al. 2004; Bani et al. 2014).

3.1 Common Steps of Pedogenesis on Ultramafic Bedrock

Olivine in the bedrock is not only weathered to clay minerals but a significant fraction transforms into Fe-oxyhydroxides with loss of Si and Mg. Formation of secondary 2:1 clay is the main difference between serpentinized and non-serpentinized ultramafic bedrock (Alexander 2009). The influence of draining conditions seems to strongly influence the outcome of pedogenesis: formation and accumulation of Fe- or Mg-rich smectite under poorly drained conditions (Lee et al. 2004; Bani et al. 2014), or

Table 1 Soil types derived from serpentinite according to the location, climatic conditions, mineralogy of the bedrock and position in landscape

Bedrock	Climate	Location	Mineralogy (order of predominance)	Soil type (WRB soil resources) (as described or adapted from descriptions)	References
Serpentinite	Semi-continental	Slovakia	Serpentine, magnetite	Technosol (hypermagnesic)	Massoura et al. (2006)
Augite-serpentinite	Sub-alpine	Swiss Alps	Serpentine, augite, spinels	Dystric Cambisol—rock slides	Gasser et al. (1995)
Serpentinite	Sub-alpine	Italian Alps	Serpentine, magnetite	Haplic Regosol (dystric)—mid-slope	D'Amico et al. (2008)
«	«	«	«	Epileptic Cambisol (protospodic)—high-solpe	«
Serpentinite	Temperate montane	Poland	Serpentine, spinels	Eutric cambic Leptosol (magnesic)	Kierczak et al. (2016)
Serpentinite	Semi-continental	Poland	Serpentine, spinels	Eutric skeletic leptic Cambisol (magnesic)	Kierczak et al. (2016)
Serpentinite	Semi-continental	Austria	Serpentine, chlorite, spinels	Skeletic hypereutric Leptosol (hypermagnesic)	Hseu et al. (2018)
Serpentinite	Semi-continental	Austria	«	Eutric Leptosol (magnesic)	Hseu et al. (2018)
Serpentinite	Temperate oceanic	France, Centre	Serpentine, chlorite, magnetite	Hypereutric Cambisol (hypermagnesic)	Caillaud et al. (2004)
Foliated serpentinite	Temperate oceanic	Italy, Western Alps	Antigorite, chlorite, and magnetite	Leptic skeletic hypereutric Cambisol (hyper)magnesic	Marescotti et al. (2019)
Serpentinite	Mediterranean montane	Albania	Serpentine	Chromic hypereutric Cambisol (magnesic)—slope	Bani et al. (2014)
«	«	«	Serpentine (alluvium)	Eutric cambic Vertisol (hypermagnesic)—downslope or alluvial terrace	Bani et al. (2014), Estrade et al. (2015)
Serpentinite	Mediterranean montane	California	Serpentine (no pyroxene)	Lithic mollic Leptosol (magnesic)—summit	Alexander and Dushey (2011)
«	«	«	«	Epileptic luvic Phaeozem (magnesic)—slope	
«	«	«	«	Endoleptic Luvisol (magnesic)—downslope	«
Serpentinite	Mediterranean	Italy	Serpentine, magnetite	Leptosol (hypermagnesic)—upslope	Bonifacio et al. (1997)
«	«	«	«	Leptic Cambisol (hypermagnesic)—backslope	«
«	«	«	«	Chromic Luvisol (magnesic)—downslope	«
«	«	«	«	Dystric Cambisol (magnesic)—bottom	«
Serpentinite	Warm temperate	Japan	Serpentine	Leptic Cambisol (hypermagnesic)	Hseu et al. (2018)

(continued)

Table 1 (continued)

Bedrock	Climate	Location	Mineralogy (order of predominance)	Soil type (WRB soil resources) (as described or adapted from descriptions)	References
«		«	«	Dystric Cambisol (magnesic)	«
Serpentinite	Temperate subhumid	Mexico, Oaxaca	Lizardite, antigorite, chlorite, talc, magnetite	Rhodic hypereutric Cambisol (magnesic)	Navarrete Gutiérrez et al. (2018)
Serpentinite	Dry subtropical (tropical subhumid)	Mexico, Puebla	Lizardite, antigorite, chlorite, talc, magnetite	Hypereutric rhodic Cambisol	«
Serpentinite	Humid subtropical	Taiwan	Serpentine, chlorite, enstatite	Cambic Leptosol (magnesic)—upslope	Cheng et al. (2011)
«	«	«	«	Eutric Cambisol (magnesic)—slope	«
«	«	«	«	Haplic Luvisol—downslope	«
«	«	«	Serpentine, amphibole, talc, chlorite	Haplic Vertisol—shoulder	Hseu et al. (2007, 2018)
Serpentinite	Tropical short dry season	Brasil, Minas	Serpentine, tremolite, chlorite	Eutric Regosol (magnesic)	Vidal-Torrado et al. (2006)
Serpentinite	Humid tropical (equatorial)	Sabah	Serpentine, magnetite	Eutric mollic Leptosol (hypermagnesic)—slope	van der Ent et al. (2016a, 2018a, b)
Serpentinite	Humid tropical (equatorial)	Indonesia, Sulawesi	Serpentine, olivine, augite	Posic Ferralsol (eutric, rhodic)	Anda (2012)
Serpentinite	Humid tropical (equatorial)	Indonesia, Kalimantan	Serpentine, chlorite	(Rhodic or chromic) Acrisol (us: typic hapludult)	Hseu et al. (2018)
Serpentinite	Humid tropical (equatorial)	Indonesia, Halmahera	Antigorite, lizardite, chromite	Leptic hypereutric rhodic Cambisol (magnesic)	Lopez et al. (2019)
Serpentinite	Humid tropical (equatorial)	Cameroon	Antigorite, magnetite, (olivine)	Geric Ferralsol	Yongue-Fouateu et al. (2006)
Serpentinite	Humid tropical	New Caledonia	Not described	Eutric Cambisol (hypermagnesic) > Vertisol	Proctor (2003)

Soil types are given according to the latest version of soil taxonomy (IUSS Working Group WRB 2014)

development of low-charge vermiculite in well-drained soils (Bonifacio et al. 1997). Serpentine-group minerals are commonly unstable in soil conditions and form secondary 2:1 phyllosilicates as well (Bonifacio et al. 1997; Lee et al. 2003; Cheng et al. 2011). Iron released from olivine and serpentine during weathering can be bound in a great range of secondary minerals according to temperature and drainage conditions. Under a temperate climate and even in the case of moderately weathered tropical soils, Mg plays a leading role among exchangeable cations although Ca binds preferentially to soil Cation Exchange Capacity (CEC; Lee et al. 2001; Chardot et al. 2007; Kierczak et al. 2007; Cheng et al. 2011) despite much lower concentrations than Mg in soils. Magnesium is partially leached during soil formation in temperate

Table 2 Soil types derived from non- or slightly-serpentinized peridotite according to the location, climatic conditions, mineralogy of the bedrock and position in landscape

Bedrock	Climate	Location	Mineralogy (order of predominance)	Soil type (WRB soil resources) (as described or adapted from descriptions)	References
Hornblende-peridotite	Semi-continental	Poland	Serpentine (32%), enstatite, forsterite, amphibole	Eutric skeletic leptic Cambisol (magnesic, siltic)	Kierczak et al. (2016)
Partially serp. harzburgite	Temperate montane	France, Vosges	Serpentine, olivine, pyroxene, chlorite	Hypereutric Cambisol (magnesic)—slope	Chardot et al. (2007)
Partially serp. lherzolite	Temperate oceanic	Italy, Western Alps	Antigorite, enstatite, clinochlore, olivine	Chromic leptic skeletic hypereutric Cambisol (hyper)magnesic	Marescotti et al. (2019)
Peridotite	Mediterranean montane	California	Olivines, pyroxenes	Abruptic Luvisol—summit	Alexander and Dushey (2011)
«	«	«	«	Endoleptic chromic Luvisol—downslope	
Peridotite	Humid mediterranean montane	«	«	Ferritic Luvisol (rhodic)	Alexander (2014)
Peridotite	Humid tropical	New Caledonia	Not described	Geric Ferralsol (pisolithic rhodic)—slope and downslope	Becquer et al. (2001)
Partially serp. peridotite	Humid tropical	New Caledonia	Olivines, serpentines, enstatite	Geric Ferralsol (pisolithic)	Dublet et al. (2014)
Peridotite	Humid tropical	Philippines	Not described	Geric Ferralsol	Fan and Gerson (2011)
Dunite	Tropical montane	Malaysia, Sabah	Olivines	Dystric folic Cambisol (magnesic)	van der Ent et al. (2016a, b)
Peridotite	Humid tropical (equatorial)	«	Forsterite, antigorite, lezardite, tremolite, spinels, diopside	Plinthic rhodic Ferralsol (magnesic)	van der Ent et al. (2018a, b)
Harzburgite	Humid tropical (equatorial)	Indonesia, Halmahera	Ni-rich olivine, Enstatite, chromite, antigorite	Geric plinthic rhodic Ferralsol	Lopez et al. (2019)
Dunite	Humid tropical (lower montane)	Indonesia, Halmahera	Ni-rich olivine, chromite	Geric rhodic plinthic Ferralsol (magnesic)	«
Pyroxenite	Tropical long dry season	Brazil, Cerrado	Enstatite, serpentine, spinel	Vertic eutric Cambisol (magnesic rhodic)—backslope	Garnier et al. (2009b)
«	«	«	«	Geric Ferralsol (pisolithic rhodic)—downslope	«
Pyroxenite	Tropical long dry season	Brazil, Cerrado	Enstatite, diopside	Geric Ferralsol with smectitic saprolite	Colin et al. (1990)
Dunite	«	«	Olivines	Geric petroplinthic rhodic Ferralsol	«

Soil types are given according to the latest version of soil taxonomy (IUSS Working Group WRB 2014) climates (incomplete hydrolysis), and a variety of secondary clay phases such as vermiculite and smectite, are produced; in contrast, in tropical lateritic soils Mg is nearly totally leached (complete hydrolysis) as is Si, leading finally to the accumulation of free Fe-oxides (Becquer et al. 2001).

Ultramafic soils share a number of chemical particularities including a low Ca/Mg ratio with Ca existing at significantly lower concentrations than in other soils of surrounding areas. The ultramafic soils also typically contain elevated levels of metals other than Fe, Mn, Ni, Cr and Co, which could induce toxicity for most plants. Serpentine soils are commonly deficient in essential plant nutrients such as N, K and P (Brooks 1987; Proctor and Woodell 1975). In ultramafic soils, Cr and Ni distribution and mineral speciation strongly depend on the mineralogy of the bedrock (Garnier et al. 2006, 2009b; Raous et al. 2013), as well as on climatic conditions (Massoura et al. 2006), position in the toposequence (Cheng et al. 2011), and more precisely on thermodynamic conditions of the soils (Antić-Mladenović et al. 2011). All these factors have been evidenced in a recent thorough work on the ultramafic soil cover of Kinabalu Park in Malaysia (van der Ent et al. 2018a). Among these, the degree of serpentinization is known to be a major discriminant factor in ultramafic pedogenesis (Alexander 2004, 2009; Pędziwiatr et al. 2018; van der Ent et al. 2018a). Photographs of the most common pedons mentioned in the following paragraphs are shown in Fig. 5.

3.2 Soils on Serpentinite Bedrock

Serpentinite is one of the most amazing bedrocks for soil development worldwide because soils developed on this substrate tend to be similar in pedogenesis and functioning regardless of latitude or elevation (Table 1): They are mostly classified as Cambisols or closely-related soils (van der Ent et al. 2018a). If we take a close look at the genesis and characteristics of these soils in both cold and temperate climates, they commonly range from high pH Regosols/Leptosols with cambic properties with CEC dominated by Mg over Ca, to Cambisols with neutral to slightly acidic pH (Caillaud et al. 2004; Chardot et al. 2007; Kierczak et al. 2007, 2016). Temperate ultramafic Cambisols typically contain serpentine as the predominant mineral phase, although 2:1 clays either derive from the bedrock (e.g. chlorite) or form from serpentine weathering and related loss of Mg (Caillaud et al. 2009; Chardot et al. 2007). Formation of Fe-rich smectite from serpentine is evidenced in temperate serpentinite soils (Caillaud et al. 2004, 2009). The Mg-chlorite is weathered to trioctahedral vermiculite (Caillaud et al. 2009). During weathering, free Fe is released and oxyhydroxides are partly crystallized (Chardot et al. 2007). The chroma from serpentinite soil in temperate conditions is generally redder than that in surrounding soils developed on non-ultramafic substrates, owing to the high content of free Fe (Chardot et al. 2007), although not as high as for soils developed on non-serpentinized peridotite (Kierczak et al. 2016; Marescotti et al. 2019).

In Mediterranean conditions, weathering intensity is higher and magnesic Cambisols have been shown to form after the loss of 85–90% of the initial bedrock material (Estrade et al. 2015). Also, further pedological evolution may occur if topographic conditions are suitable, including the formation of Luvisols where the pedons are thicker (Bonifacio et al. 1997). However, the soils remain dominated by magnesic Cambisols where landscapes are dominated by slopes. As in temperate environments (Caillaud et al. 2004, 2009), the primary serpentine is easily weathered to smectite (Bonifacio et al. 1997) that typically is Fe-rich (Ece et al. 1999; Caillaud et al. 2004; Bani et al. 2014). Further evolution of the soil transforms smectite into low-charge vermiculite if drainage conditions of the soil are favourable (Istok and Harward 1982; Bonifacio et al. 1997). In the absence of sufficient drainage (downslope or in alluvial zones), Vertisols form due to a significant accumulation of neoformed smectites (Lee et al. 2003; Bani et al. 2014), some of which are Mg-rich smectite that is not found in Cambisols (Bani et al. 2014). Upslope, the soil cover

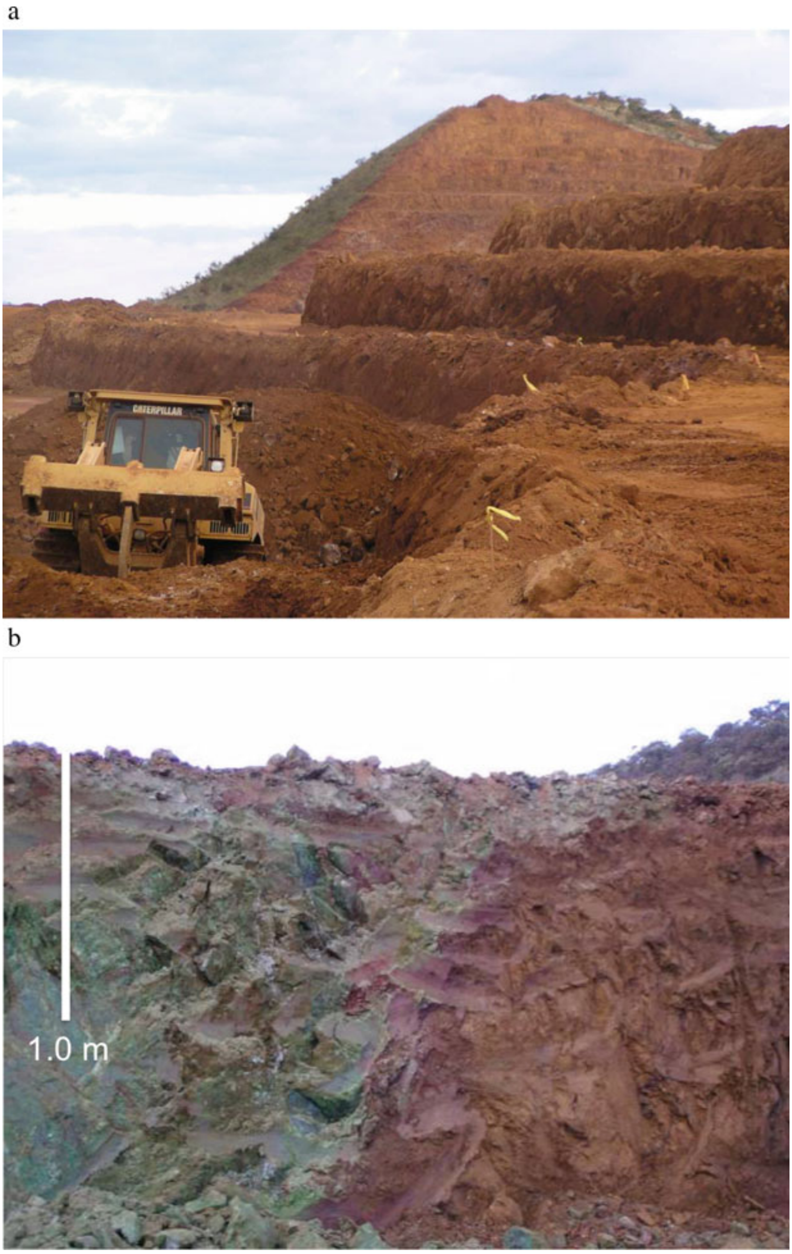

Fig. 5 **a** Formation of hematite on the upper part of the lateritic profile in the background hill due to surface dehydration of Fe oxyhydroxides (Niquelândia, Brazil). **b** A fault between pyroxenite (left) and dunite (right) allows seeing the difference of composition and mineralogy: Ni-rich smectites (left) and goethite (right) (Niquelândia, Brazil). Photographs: G. Echevarria

is still very similar as in colder regions (Bonifacio et al. 1997; Alexander and DuShey 2011), and Leptosols are still found on shallower portions of the toposequences (Marescotti et al. 2019).

In humid climates of subtropical to tropical areas, serpentinite soils are dominated by 2:1 clays (e.g. smectite) and mostly dominated by Cambic Leptosols/Cambisols having a relatively high pH and magnesic/hypermagnesic properties

(Cheng et al. 2011; Isnard et al. 2016; van der Ent et al. 2016b). These soils are typically developed on upslope and midslope landscape positions (Hseu et al. 2007, Cheng et al. 2011). Within these soils, the main pedogenic process is weathering of primary clay minerals (i.e. serpentines) to smectite after a significant loss of Mg (Hseu et al. 2007; Nguyen Thanh et al. 2017) and formation of a stable organo-mineral complex. As in temperate ultramafic soils di-octahedral Fe-rich smectites are usually formed, except in soil bottom layers with poor drainage and higher Mg contents (Nguyen Thanh et al. 2017). Vertic properties have been mentioned in many ultramafic Cambisols in such regions, because of the high proportion of 2:1 clays (e.g. smectite), including even the formation of Vertisols sensu stricto (Proctor 2003). Soils tend to be rejuvenated because of the Vertic properties and erosion where a slope is present; that could explain the predominance of Cambisol-related soils even in humid-tropical conditions. Under conditions that are favourable for leaching, the loss of Si from smectite/vermiculite can lead to accumulation of kaolinite and Fe-oxides (Hseu et al. 2007). Luvisols or other tropical leached soils (e.g. Acrisol) are present in such areas (i.e. downslope) where weathering products of the toposequence accumulate (Hseu et al. 2007, 2018; Cheng et al. 2011), which again shows a great similarity with those of colder regions (Bonifacio et al. 1997). Only one record of a Ferralsol has been reported to develop on pure serpentinite, in Sulawesi (Anda 2012), but the author did not mention if lateritic material had accumulated from the surrounding soil cover on peridotite, or if that particular soil was several millions of years old. According to Gleeson et al. (2003), laterite formation on wholly serpentinized peridotite is common and leads to smectite-rich saprolite owing to poor drainage of the serpentinite. The presence of deep Geric Ferralsols with possible accompanying ferricrete is reported on serpentinite that contains only traces of olivine (Yongue-Fouateu et al. 2006). The deep laterite profiles developed on this 240 km^2 outcrop in the Equatorial Forest in Cameroon have probably developed under stable climatic conditions for tens of millions of years; lateritization is still active. If the presence of serpentinite reduces the speed of lateritization, the endpoint of pedogenesis on ultramafic material (serpentinized or not) seems to be the formation of Petroplinthic Geric Ferralsols. However, this type of soil is seldom found in tropical regions because many local factors apparently block pedogenesis at an early stage (e.g. steep slopes, Vertic properties).

3.3 Soils on Non-serpentinized Peridotite

It is difficult to differentiate ultramafic soils developed on serpentinite versus peridotite in cold environments (Kierczak et al. 2007, 2016) because their geochemistry is generally similar and the end products of weathering (i.e. soils) do not differ much in chroma, soil depth, and weathering intensity. However, there are detectable differences in soil mineralogy and composition (Pędziwiatr et al. 2018). In warmer climates, the differences become more obvious (Alexander and DuShey 2011; van der Ent et al. 2018a) and in tropical environments, we face two different ecosystems (Proctor 2003; van der Ent et al. 2018a). Cuba is a good example, where Cambisols occur on serpentinites that are covered with maquis-like vegetation (high occurrence of Ni-hyperaccumulators); Ferralsols occur on peridotites, which host a rainforest. Unlike Cambisols on serpentinite, ultramafic Ferralsols generally contain very few hyperaccumulator species (van der Ent et al. 2018a).

In temperate environments, the predominant soil type on non- or slightly serpentinized peridotite is again Cambisol (Table 2) that displays slight differences with Cambisols developed on serpentinite (Pędziwiatr et al. 2018). One such difference is the qualifier ‘chromic’ that can be applied as a consequence of iron segregation (easily weatherable olivine can produce significant amounts of Fe-oxyhydroxides). Soil Chroma of these soils can be typical of those found on Mediterranean soils with values situated in the YR range (whereas surrounding soils are in the Y range), locally reaching YR 7.5 or redder (Chardot et al. 2007; Kierczak et al. 2016). In soils developed on serpentinite bedrock, the amount of 'free' Fe-oxides (amorphous and crystalline) measured by dithionite-bicarbonate-citrate extraction (McKeague and Day 1966) is significantly different from that of surrounding soils formed on other types of bedrock and can exceed 5% (Chardot et al. 2007). Also, the proportion of smectite in Bw horizons of peridotite derived Cambisols is less than in soils formed on serpentinite (Caillaud et al. 2004; Chardot et al. 2007).

In Mediterranean environments, Fe segregation becomes a significant pedogenic process on peridotite (Alexander and DuShey 2011). Amounts of free Fe in the well-drained soils of the Klamath Mountains transect (i.e. a typical ultramafic region of northern California) are related to the degree of serpentinization of the parent peridotite and its weathering extent (Alexander 2014). Goethite in the peridotitic soil is predominant in the wetter soil having higher free Fe contents (Alexander 2014). In the peridotitic soil, the accumulation of Fe-oxyhydroxides (up to 25%; Massoura et al. 2006; Alexander 2014) is associated with chroma values redder than YR 5; the soils can be defined as Chromic. Such soils are mostly Luvisols with properties that typically include Magnesic and Chromic/Rhodic. The high amount of free Fe, and the reduced concentrations of 2:1 clay minerals in the B horizons of these soils, induce the lack of CEC with net positive charges such as in Ferralic horizons that are typical of tropical lateritic soils. This feature found in Mediterranean climatic conditions on peridotite is unique for non-tropical soils (Alexander 2014) and means that pedogenesis on peridotite under Mediterranean conditions involves the first steps of lateritization.

Soil genesis on peridotite in tropical environments is probably the most peculiar and intense type of weathering of rock occurring on the surface of Earth. It has been extensively documented over the last 40 years because of the economic value of nickel laterites (Trescases 1975; Nahon et al. 1982; Colin et al. 1990; Gleeson et al. 2003). Ultramafic laterites are divided into three main categories that mostly differentiate in the saprolitic horizon, although the type of Ni laterite deposit is only partially controlled by lithology (Gleeson et al. 2003). Each of the three laterite classes may be developed on peridotite, but on dunite protoliths oxide deposits predominate. However, in terms of soil properties, these three types present only slight differences as all are classified as Geric Ferralsols. Only a few papers have focused on biological and active soil functioning at the toposequence level that provide elements of soil taxonomy (Becquer et al. 2001; Garnier et al. 2009b). Most ultramafic laterites studied worldwide are paleo-laterites that are not actively forming, such as Cuban or Dominican ultramafic laterites that developed in the Tertiary (Aiglsperger et al. 2016). Below we therefore emphasize on soil behaviour rather than trying to describe the complete formation and evolution of laterites. Some of the most developed ultramafic laterite profiles result in 60–100 m (Colin et al. 1990) of weathered material with the formation of a full lateritic horizon, i.e. goethite-dominant limonite that ranges in thickness from 4 m in Niquelândia (Brazil) on pyroxenite (Colin et al. 1990) to 30 m in Goro (New Caledonia) on peridotite (Dublet et al. 2014), or in Moa Bay (Cuba) on non-weathered harzburgite (Aiglsperger et al. 2016). On pyroxenite, the high silica content (twice as high as in other peridotite) allows the formation of smectite at a relatively shallow depth (Fig. 6b) and therefore limits the development of laterite. Such soils are relatively similar to those found on serpentinite where smectite minerals predominate (Gleeson et al. 2003; Garnier et al. 2009b), also showing a high CEC (high proportion of 2:1 clays) that is incompatible with Ferralic and Vertic properties due to the swelling-shrinking properties of smectite.

In the lateritic horizon usually described by miners as 'limonite' or 'laterite', the mineralogy is dominated by goethite. Hematite is formed at the surface ('red limonite or laterite') as a consequence of extremely hot temperatures reached at the soil surface where affected by sunlight (Fig. 5a). Mineralogical and geochemical changes of iron oxides occur throughout the thickness above the bedrock (Dublet et al. 2014). The formation of ferricrete (iron pan) after crystallisation (Fig. 3e) and dehydration of Fe-oxides

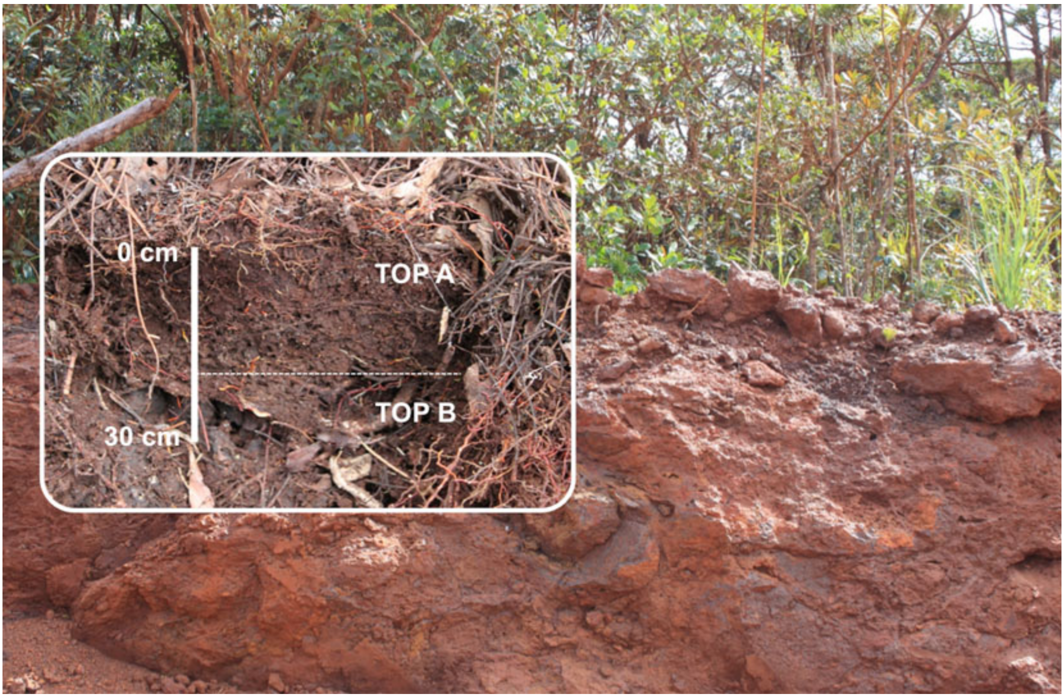

Fig. 6 Hyperskeletic mollic sideralic Leptosol on ancient laterites with a stunted forest dominated by *Gymnostoma* species (Goro, New Caledonia). Photographs: G. Echevarria

(typically as a result of successive dissolution-crystallization cycles during lateritization) results in a significant loss of Ni (Dublet et al. 2015) and a relative gain of trivalent elements (e.g. Al, Cr, Sc), especially in hematite particles (Aiglsperger et al. 2016). Where developed on dunite, the ferricrete can be continuous with hematite being the predominant mineral, whereas goethite is a secondary phase (Colin et al. 1990). On olivine-poor ultramafic bedrock, the formation of ferricrete does not seem to be significant (Colin et al. 1990). Ferricrete dominates in the southeastern part of the main island of New Caledonia where it is continuous over many square kilometres (Fig. 6). The formation of ferricrete is the final evolution of Petroplinthic Rhodic Geric Ferralsols and, after the sealing of soil surfaces, a landscape of Hyperskeletic Leptosols (Quintela-Sabarís et al. 2018), a few decimetres deep, develops on a large scale. A rather low vegetation (stunted secondary forest dominated by *Nothofagus* spp., *Arillastrum gummiferum*, and *Gymnostoma* spp.) develops on these soils (Isnard et al. 2016) where most of the nutrients are brought to plant roots by the recycling of decayed organic matter.

4 Mining Ultramafic Technosols

After removing the lateritic cover, mining operations are required to rehabilitate the stripped areas by preferentially using the spoil materials (Echevarria and Morel 2015; Quintela-Sabarís et al. 2018). The construction of mining Technosols aims at restoring the soil cover in order to fulfil essential ecological and environmental functions (Echevarria and Morel 2015). Ultramafic raw materials (spoils, stripped soils, tailings) are the main geochemical driving force of the new soil cover. Limonitic spoils composed mainly of goethite and hematite, and saprolitic spoil composed of a high fraction of clay minerals and chalcedony, are the main materials available for soil construction (Raous et al. 2013). Topsoil is also frequently used to cover the spoil materials after storage, for periods that may vary from a few days to several years (Echevarria and Morel 2015). The evolution of topsoil biogeochemistry and biology during storage has been thoroughly studied in a recent project called BIOTOP, which was funded by the New Caledonian Research Centre on Nickel (CNRT). The evolution of topsoil geochemistry after stripping and storing (0–24 months) showed several trends. Storage of topsoil developed on ferricrete does not affect strongly its chemical and biochemical fertility (Echevarria and Morel 2015; Quintela-Sabarís et al. 2018). Typically, organic amendments or even mineral fertilizers (hydroseeding) are also added for the reconstruction of soil cover on stripped land.

Globally, Serpentinite quarries are also in need of environmental rehabilitation and the constructed soil cover is strongly influenced by the chemical and mineralogical properties of serpentinites: high pH, high Mg/Ca ratios, lack of nutrients (Massoura et al. 2006; Cerdeira-Pérez et al. 2019; Quintela-Sabarís et al. 2019). Efforts to create new soil covers (Technosols) are currently being carried out, either by understanding the natural succession of spontaneous plants that re-colonize the mineral barrens (Quintela-Sabarís et al. 2019) and anticipate their needs to speed up revegetation, or, by planting Ni hyperaccumulator plants in order to implement Ni phytomining as well as to improve soil fertility (e.g. microbial functions, nutrient availability, organic matter content) (Cerdeira-Pérez et al. 2019).

5 A Global Model of Ultramafic Soil Evolution

Summarizing the pedogenetical features of all soils developed on ultramafic bedrock worldwide cannot be done on a single figure. However, in most sites from cold to tropical climates, it is possible to highlight the most significant pedogenic processes and predominant mineral phases that characterise the ultramafic soils known on both non-serpentinized peridotite and serpentinite (Fig. 7). A comparison of the different evolutionary patterns developed in cold, temperate, and Mediterranean regions, based on results from the literature, showed that Mg is extremely depleted and reduces from nearly 20% of the mass of the bedrock to less than a few percent (Kierczak et al. 2007). Silicon is also depleted, especially in Mediterranean conditions. As a result, the relative concentrations of Fe and Cr increase in the soil (with a strong impact on soil redness), as well as those of other stable metals (i.e. Ti and Nb), whereas Ni is slightly depleted relatively in temperate soils and is stable in Mediterranean soils. Importantly, 85–90% of the Ni is lost during pedogenesis (Estrade et al. 2015). The presence of serpentine considerably reduces the loss of Si, and most mineral phases will be primary and secondary clay minerals.

6 The Fate of Nickel During Ultramafic Soil Evolution

Nickel in ultramafic bedrock is borne in serpentine, olivine, and pyroxene grains with an average concentration of 1200 to 3800 $\mu g\ g^{-1}$ for serpentine (Table 3). In serpentine clays, it is located in the octahedral sheet (Siebecker et al. 2018). In magnesic Cambisols and related soils, soil organic matter (Hseu et al. 2018), poorly crystallized Fe-oxides (Chardot et al. 2007), possibly Mn-oxides (Alves et al. 2011), and secondary 2:1 clays such as Fe-rich smectite (Bani et al. 2014) will hold most of the Ni in the soil. However, weathered serpentines will contain higher concentrations of Ni than those, intact, present in the bedrock, i.e. 6000 $\mu g\ g^{-1}$ (Bani et al. 2014). Progressively, the formation of smectite produces Ni-rich particles that may in places reach several weight percent (Table 3), including under non-tropical conditions (Bani et al. 2014). Where lateritization occurs, Ni from the first few meters is leached down the profile where Fe-oxides crystallize, and is then transferred to clay minerals in deep saprolite (Colin et al. 1990; Dublet et al. 2014). These saprolite clays that trap Ni can be smectite (Colin et al. 1990; Raous et al. 2013), talc (Becquer et al. 2006), or serpentine (Dublet et al. 2012). On top of the saprolite layer, Mn oxides (e.g. asbolane,

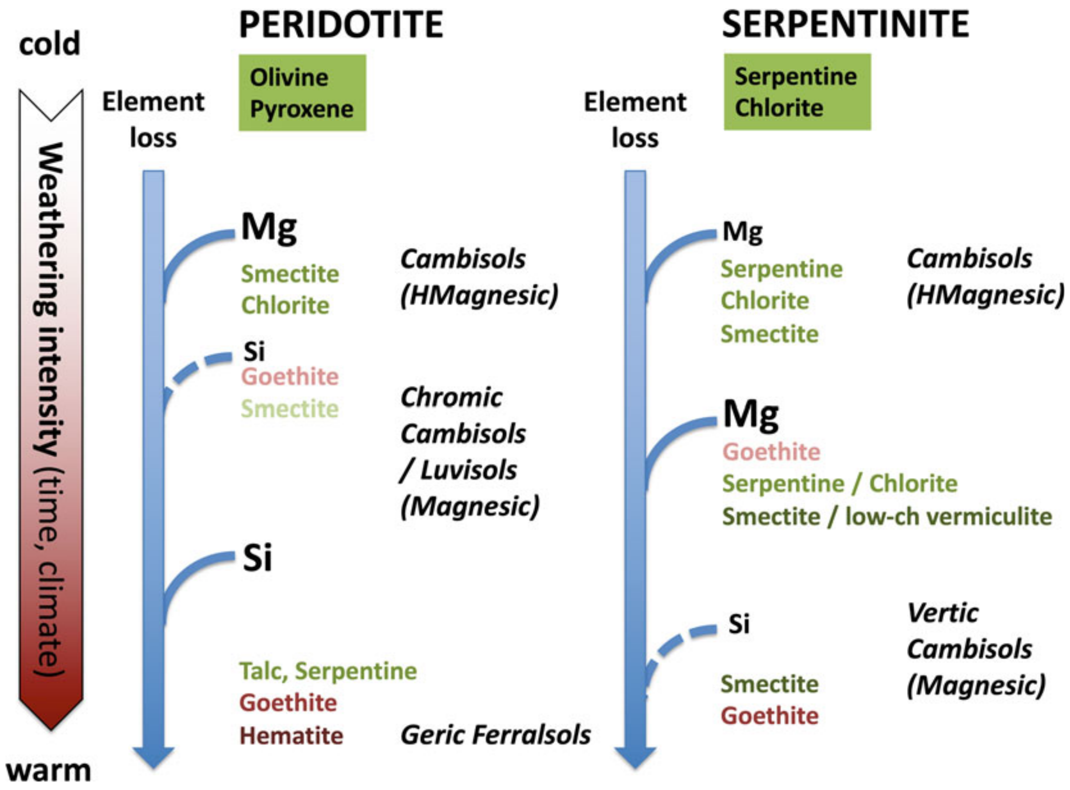

Fig. 7 A simplified description of soil genesis and evolution on ultramafic bedrock: non-serpentinized peridotite and serpentinite. In warmer climates, the difference between the two types of ultramafic bedrocks becomes more pronounced. The high abundance of serpentine minerals impedes the formation of a lateritic (Ferralic) horizon and gives to the soil Cambic and Vertic properties, mainly inherited from the high proportion of smectites. Pyroxenite will produce a similar type of pedogenesis than serpentinite

lithiophorite) may also trap Ni and Co (Llorca and Monchoux 1991; Dublet et al. 2014). However, Ni is also concentrated in goethite from the yellow limonite horizon that has not undergone such pervasive dissolution-recrystallization processes (Dublet et al. 2015).

7 Nickel Availability in Ultramafic-Bearing Minerals and Soils

7.1 Methods of Evaluating Nickel Availability

Current methods to assess and characterize Ni chemical availability in ultramafic soils are described by numerous workers (Echevarria et al. 1998, 2006; Chaney et al. 2005; Garnier et al. 2006, 2009a; Raous et al. 2013; Zelano et al. 2016a, b; van der Ent et al. 2018b), and include:

- Single chemical extractions using salts—$CaCl_2$ and $Sr(NO_3)_2$;
- Single chemical extractions using chelating agents—DTPA and EDTA;
- Sequential chemical extraction procedures; and
- Isotopic exchange and dilution techniques (IEK).

The last techniques are useful and complete tools for measuring the true phytoavailability of trace elements in soils (Echevarria et al. 1998; Massoura et al. 2004). Measured by IEK, isotopically exchangeable Ni during time t (E_t) refers mostly to the element retained through

Table 3 Element concentrations in leaves, litter and soils under the influence of the Ni-hyperaccumulator *Odontarrhenia chalcidica* grown on a Eutric Vertisol (Hypermagnesic) in Albania

Compartment	Nickel (g kg^{-1})	Calcium (%)	Potassium (%)
Leaves	19.0	3.57	1.50
Litter (current year)	9.22	2.06	0.53
Soil under litter at 0–3 cm	3.03 a	0.72 a	0.34 a
Bare soil (no litter) at 0–3 cm	2.84 b	0.69 a	0.32 a

Mean values of five replicates that are followed by different letters indicate a significant difference at the $p < 0.05$ level (ANOVA)

sorption and surface-complexation onto soil particles. Soil labile Ni − E_t—is highly dependent on the chemical state of the element, i.e. inclusion in crystal lattices (Massoura et al. 2006; Zelano et al. 2016a, b). The metal exchanged for a very short period of time ($E_{0\text{–}1\ \text{min}}$) corresponds to the fraction that is weakly bound to the soil solid phase (e.g. CEC). Isotopically exchangeable pools having longer periods of exchange (i.e. 1 min to 3 months) are typically linked to diffusion-limited sorption sites (Massoura et al. 2006; Zelano et al. 2016b).

The DTPA extraction of Ni in soils is a good field test for assessing ecotoxicological risk (L'Huillier and Edighoffer 1996; Echevarria et al. 1998, 2006; van der Ent et al. 2018b). The Ni pool extracted by DTPA was significantly correlated with medium-term, isotopically exchangeable, i.e. $E_{0\text{–}3\ \text{months}}$, which is the same source of Ni uptake for plants with contrasted demand for Ni (Echevarria et al. 2006). Recently, it was shown that DTPA-extracted Ni has a similar stable isotope composition as soluble Ni, whereas soil Ni has a much lighter isotope composition (Estrade et al. 2015). The DTPA extraction thus accesses only exchangeable and surface-complexed Ni that is eventually available and accessible to plants (Echevarria et al. 1998).

In 100 very contrasted soil samples that represent a range of origin and total content of Ni in soils worldwide, including ultramafic soils, IEK methods and DTPA extractions have shown that availability of Ni to plants is mainly controlled by soil pH (Echevarria et al. 2006). As expected, soil pH controls the intensity (i.e. Ni concentration in solution). In 16 naturally and anthropogenically Ni-rich soils selected from various weathering conditions, Ni was found to be present in either primary phyllosilicates (i.e. serpentine, chlorite, talc), secondary clay minerals, or Fe–Mn oxyhydroxides (Massoura et al. 2006; Echevarria et al. 2006). The availability of Ni from primary clay minerals was low and attributed to the presence of Ni within the crystal lattice (Zelano et al. 2016b). Nickel in secondary clay minerals (e.g. smectite) was probably sorbed onto the mineral surfaces with the result that its availability was very high (Massoura et al. 2006; Raous et al. 2010, 2013). Bioavailability of Ni in goethite-dominant soils was extremely poor, because these minerals act as a stable sink for the metal in both natural and contaminated Ni-rich soils (Massoura et al. 2006; Raous et al. 2010; 2013; Zelano et al. 2016a, b). The response of excluder, accumulator, and hyperaccumulator plants to Ni availability assessed by IEK methods showed that all plants took up Ni from the same labile pools of Ni in soils, regardless of the mechanisms of root uptake, translocation and storage (Massoura et al. 2004; Echevarria et al. 2006). This finding validates IEK as a universal method for assessing Ni availability in soils and other environmental solid matrices (Zelano et al. 2013, 2016a).

7.2 Main Ni-Bearing Phases in Ultramafic Soils and Ni Availability Properties

The use of isotope exchange kinetics to describe Ni availability properties of pure Ni-bearing minerals was introduced 15 years ago (Echevarria et al. 2006; Massoura et al. 2006), as Ni-bearing phases in ultramafic soils were shown to be nearly the sole control on Ni availability, with only a limited effect imposed by pH. The Ni availability properties of single pure minerals were described for chrysotile, which was purified from an asbestos mine spoil (Chardot-Jacques et al. 2013), and for Ni-rich synthetic goethite (Massoura 2003), and fully explained the resulting Ni transfer to plants in both cases. Recently, Zelano et al. (2016a) detailed isotopically exchangeable properties of single pure mineral phases that are commonly found in ultramafic soils, with E_t values being a first-order kinetic of time, and specific for each Ni-bearing phase. Furthermore, these workers modelled the bulk Ni availability of soils by computing the linear combination of properties of single minerals according to their relative proportion in the studied soils (Zelano et al. 2016a). It was verified, in most cases, that the computed values were accurate and that Ni-bearing phases contributed to soil Ni availability in this manner. This approach was successfully applied to natural ultramafic soils and the mining of Technosols (Zelano et al. 2016b), thus assigning to each phase its contribution in Ni availability.

No study has been performed on primary olivine and pyroxene assuming that the only release of Ni from these silicates comes from their dissolution (Chardot-Jacques et al. 2013; Pędziwiatr et al. 2018). Serpentine minerals in unweathered bedrock have been reported to contain from 0.12 to 0.38 wt% Ni (Caillaud et al. 2009; Yongue-Fouateu et al. 2006; Quantin et al. 2008; Bani et al. 2014; Kierczak et al. 2016), with a surprisingly high value of 1.99 wt% reported in specific conditions (Quantin et al. 2008). In cold temperate conditions, the serpentine Ni content in the Bw horizon remains similar to that in the bedrock: 0.18 wt% (Chardot et al. 2007). However, in the B horizons of Cambisols and Vertisols developed on serpentinite under Mediterranean conditions, it seems that the Ni content in serpentine minerals is slightly higher (e.g. 0.60–0.85 wt%) than in the original bedrock (0.30 wt%), probably because these serpentines have undergone incipient weathering (Bani et al. 2014). In the saprolite layers of Geric Ferralsols, serpentine minerals such as nepouite and garnierite can contain up to 20 wt% Ni as a result of neoformation (Fig. 3d). The availability of Ni in primary phyllosilicates such as chrysotile is very limited (Chardot-Jacques et al. 2013); when equilibrated with water, these minerals release Ni concentrations in solution that are very low at *ca.* a few µg L^{-1}, exchangeable sites that are very limited (a few % of total Ni), and a strong diffusion-limited component that slowly releases soluble and exchangeable Ni over time (Zelano et al. 2016a). Where plants are grown on this sole substrate, Ni absorption by roots is mainly fed by chrysotile dissolution instead of by labile pools (Chardot-Jacques et al. 2013).

Chlorite and talc in ultramafic soils can be both primary (Lee et al. 2003) or secondary (Becquer et al. 2006) minerals. Primary minerals in soils being the minerals derived from the bedrock or parent material, and secondary minerals the minerals that are transformed or neoformed during pedogenesis. Talc is a 1:1 clay mineral that is extremely resistant to pedological weathering and in places is the only clay mineral present in Ferralic horizons of ultramafic laterites (Becquer et al. 2006). The CEC of such talcs is almost null, which explains that the availability of Ni in talc (e.g. deweylite) is so scarce that it is lower than that of chrysotile (Zelano et al. 2016a). The availability of Ni in chlorite minerals is more than twice that of chrysotile (Zelano et al. 2016a), as it is a 2:1 clay mineral having much higher CEC. Although more common at the surface than in the Bw and C horizons of Hypereutric Cambisols in the Vosges Mountains of France (Massoura et al. 2006; Chardot et al. 2007), Ni availability is much higher in the lower horizons and negatively correlates with chlorite content. Chlorite is, therefore, not a significant contributor to Ni availability in ultramafic soils (Massoura et al. 2006).

Smectite is a high-exchange, high-specific, surface secondary clay. The Ni content of smectite in ultramafic soils is also highly variable and no specific trend in terms of geochemical composition (Mg-rich vs. Fe-rich), weathering intensity, or climatic conditions seems to influence the Ni content. Nickel concentrations in smectite range from 0.49–3.12 wt% in

Temperate B horizons (Caillaud et al. 2009; Bani et al. 2014), whereas the range is 0.40–14.9 wt% in a tropical Bw horizon of a Cambisol developed on pyroxenite (Garnier et al. 2009b). In the saprolite horizons of Geric Ferralsols, Ni contents typically range from 1.06–1.33 wt% (Yongue-Fouateu et al. 2006; Raous et al. 2013), as in temperate soils. But concentrations can exceptionally reach 13.3–25.9 wt% Ni in Fe-rich smectite of Geric Ferralsols developed on pyroxenite in Niquelândia, Brazil (Decarreau et al. 1987). Nickel-bearing smectite is a major source of available Ni in ultramafic soils (Bani et al. 2007; Raous et al. 2013; Zelano et al. 2016a), and its availability is like that of Mg released under similar conditions (Raous et al. 2010). The concentration of Ni measured in solution during IEK of smectite is one of the highest of all Ni-bearing minerals, amounting to 0.25–0.5 $\mu g\ L^{-1}$ (Massoura 2003; Bani et al. 2007). Instantaneously exchangeable pools (i.e. E0-1 min) are also the highest, reaching more than 100 $\mu g\ g^{-1}$ after 1 min (Massoura 2003; Bani et al. 2007; Zelano et al. 2016a) as a result of the high content of exchangeable Ni present in the CEC (Raous et al. 2013).

Iron- and Mn-oxyhydroxides are important scavengers of Ni in ultramafic soils. Where free Fe is released during the first stages of weathering, Ni is rapidly sorbed onto, and incorporated into, amorphous Fe-hydroxides (Chardot et al. 2007). Where goethite (a significant mineral in ultramafic Cambisols) is formed, the affinity to Ni seems to decrease (Massoura et al. 2006; Chardot et al. 2007; Bani et al. 2009) and the ratio of Nio/Nid is usually the double as Feo/Fed (Chardot et al. 2007); however, Ni contents in goethite can range from 0.8–4.3 wt% in these soils. Goethite in the lateritic horizons of Geric Ferralsols range from 1.7 wt% Ni% in upper layers to 3.8 wt% in deeper parts of the Ferralic horizon (Becquer et al. 2006). The same concentrations have been reported in other Geric Ferralsols (Yongue-Fouateu et al. 2006). Nickel concentration in Fe-oxides decreases from the bottom of the Ferralic horizons up to the surface, by about a factor 5–10 as a result of goethite aging (Dublet et al. 2015), a process involving dissolution and recrystallization. Hematite particles are even poorer in Ni than the surface goethite (Raous et al. 2013). The isotopically exchangeable pools of Ni in ultramafic soils were shown to correlate with concentrations of amorphous Fe-oxyhydroxide or with the ratio of amorphous to well-crystallized Fe-oxides (McKeague and Day 1966; Massoura et al. 2006). Manganese oxides, although a minor phase quantitatively in temperate soils, also may have significant concentrations of Ni that are suspected to be highly available (Alves et al. 2011). In some ultramafic areas of Serbia, the soils with highest available Ni are also those with highest available Mn (Mišljenović et al. 2018). In tropical laterites, Mn-oxides play a significant role in that Ni-bearing minerals and heterogenite can hold up to 20 wt% Ni, followed by lower Ni contents within lithiophorite and asbolane (Llorca and Monchoux 1991; Decrée et al. 2015). These minerals are the most important scavengers for cobalt; however, little is known about Ni availability in such well-characterized Mn-oxides.

Amorphous Fe-oxides are not easily isolated in pure form from bulk soils, so it is impossible to assess the specific availability of Ni in these phases. The available properties of Ni borne by goethite particles have been studied by several workers (Massoura 2003; Raous et al. 2013; Zelano et al. 2016a, b). Nickel availability associated with synthetic goethite can be nearly null (Massoura 2003), with no proof of isotopic exchange between Ni included in the crystal lattice and free Ni present in solution. This is confirmed by the absence of Ni in the CEC of limonite where Ni is contained mostly in goethite particles (Raous et al. 2013). Goethite has some potential to bear isotopically exchangeable Ni as surface-complexed Ni (Raous et al. 2013; Zelano et al. 2016a). However, Ni availability associated with synthetic goethite is extremely low relative to other ultramafic Ni-bearing phyllosilicates (Zelano et al. 2016a). Unsurprisingly, the availability of Ni from hematite is null (Zelano et al. 2016a).

Available Ni (DTPA-extractable) is strongly positively correlated to organic C in an ultramafic toposequence in Albania (Bani et al. 2014). The labile pool associated with organic matter in a Brazilian ultramafic soil also accounts for most isotopically exchangeable Ni of the whole soil, as 3 wt% of the soil mass provides 60 wt% of labile Ni (Zelano et al. 2016b). Little attention has been devoted to the role of organic-borne Ni in ultramafic soils, but recently it was shown that plants and litter are a major contributor to total Ni in surface soils (Estrade et al. 2015), which is in turn highly available. It is, therefore, crucial to describe better the pools of available Ni associated with organic matter and detail the speciation of Ni and the chemical bounds that may exist to organic matter.

8 Biogeochemical Cycling of Nickel in Ultramafic Soils

The use of nickel stable isotopes has recently been introduced in studies of ultramafic environments to elucidate the pathways and mechanisms of nickel biogeochemistry (Estrade et al. 2015; Ratié et al. 2015, 2019): mineral weathering, nickel fluxes, root uptake and plant translocation. Typically, the weathering of primary minerals during pedogenesis induces a loss of heavy isotopes by leaching processes, such that the resulting soil has isotopically lighter Ni than the parent bedrock. In several ultramafic soils, the soluble and available (i.e. DTPA-extractable) fraction of Ni is usually much heavier, isotopically, than Ni in the soil solid phase (Estrade et al. 2015; Ratié et al. 2015; Pędziwiatr et al. 2018). In a Chromic Cambisol, the upper A1 (0–3 cm) horizon presents a significantly lower degree of isotopic fractionation from bedrock than the deeper horizons (i.e. A/Bw and Bw). Similar observations were made on a Eutric Skeletic Cambisol on Serpentinite from Poland (Pędziwiatr et al. 2018) whereas a Eutric Leptosol from a partially serpentinized peridotite showed a continuous loss of available Ni in the surface, probably in relation to an intense weathering of Ni-bearing phases and a lack of CEC traps (lacking secondary high-charge clays) to prevent from the leaching of the heavier soluble fraction of Ni released during the dissolution of olivines (Pędziwiatr et al. 2018). The isotopic compositions of Ni in litter are all heavier than in corresponding rhizosphere soils, suggesting a significant contribution from decaying plant material that contains a much greater proportion of isotopically heavy Ni than the bulk soil (Estrade et al. 2015; Ratié et al. 2019). The reason for this is that plants take up soluble Ni from the soil, which is the heaviest isotopic pool of Ni present within the soil. In a ploughed ultramafic Vertisol, this relationship could not be observed because the organic matter residues in this soil are diluted in the Ap horizon (0–20 cm).

In May 2013, five plants of the Ni-hyperaccumulator species *Odontarrhena chalcidica* (syn. *Alyssum murale*) were sampled at flowering stage on a Eutric Vertisol (Hypermagnesic) in Prrenjas (Albania) where no other vegetation had grown for at least 12 months. Plants were distant from each other with at least a 1 m spacing distance (details in Bani et al. 2015). In this study, a careful sampling of plant leaves, deposited as litter beneath each plant, and surface soil samples clear of any litter particles (from a 0–3 cm depth), was carried out. In parallel, soil samples (from a 0–3 cm depth) were taken randomly in bare soils at a minimal distance (2 m) from each plant to ensure that there would be no influence of *O. chalcidica* on the geochemistry of the soil sample. All plant and litter samples were analyzed for total element concentrations after complete digestion with concentrated HNO_3. Soil samples were digested with concentrated HF for total dissolution of minerals. Digestion solutions were analyzed using ICP-MS after appropriate dilutions. The results (Table 3) clearly showed that total Ca, K, and Ni were significantly enriched in the soil beneath *O. chalcidica* after only one growth cycle of the plant (9–12 months). Moreover, the Ni contained in plant leaves after decayed material was leached away after only a few months (by almost 50%), which was the time equivalent to the age of the deposited litter. Potassium was even more affected by leaching (>66% of initial K). This experiment brings additional understanding to what had been previously shown with stable isotope studies on Ni in topsoil and litter (Estrade et al. 2015): the contribution of plants to the building up of Ni concentrations in topsoil. Furthermore, the majority of Ni present in the primary minerals is leached during pedogenesis (Kierczak et al. 2007; Estrade et al. 2015), thus resulting in a Ni pool that is enriched in lighter isotopes. Hence the existing Ni contents in topsoils, which have a Ni isotopic composition strongly influenced by plant recycling (Estrade et al. 2015), probably result from significant biogeochemical recycling. Nickel hyperaccumulator plants, which can be quite common in these environments, likely contribute in a major way to this phenomenon. More detailed studies should be carried out by tracing Ni fluxes using stable isotopes (Deng et al. 2016) in soil-plant systems that are representative of various edaphic situations worldwide, in order to shed more light on the importance of Ni biogeochemical cycling in ultramafic soils and related ecosystems.

9 Conclusions: Global Trends of Nickel Availability in Ultramafic Soils

At first glance, it seems that soils developed on serpentinite are much richer in available Ni than those developed on non-serpentinized peridotite (van der Ent et al. 2016a). However, it is not that simple, because extremely well-developed Geric Ferralsols may occur on serpentinite (Yongue-Fouateu et al. 2006), at the surface of which is a very low availability of Ni. At the same time, Cambisols with extremely high Ni availability may exist on non-serpentinized pyroxenite (i.e. peridotite) (Garnier et al. 2009b). Nickel is a relatively mobile metal in ultramafic environments (Raous et al. 2010) and its resulting total concentration in most temperate and Mediterranean soils, although of the same order of magnitude as the bedrock concentration, results from the loss of more than 85% of its initial mass in the bedrock (Kierczak et al. 2007; Estrade et al. 2015; Pędziwiatr et al. 2018). It is frequently seen that Ni is as easily released and mobilized as Mg during the steps of soil weathering and pedogenesis (Raous et al. 2010; Chardot-Jacques et al. 2013; Hseu et al. 2018). The difference between these elements is the fact that Ni forms stable complexes with organic matter and Fe- and Mn-oxyhydroxides (especially amorphous Fe-oxyhydroxides). Therefore, Ni is retained in a certain number of pedological situations in which Mg is not, thus explaining differences in losses between the two elements during pedogenesis (Kierczak et al. 2007; Hseu et al. 2018). The availability of Ni in soils is therefore favoured by the following mechanisms that may occur under various edaphic conditions:

Dissolution/weathering of primary minerals holding Ni (Chardot-Jacques et al. 2013).

- Uptake of released Ni by soil humic substances before significant amounts of secondary minerals that contribute strongly to soil CEC are produced (Hseu et al. 2018).
- Building up a CEC from the neoformation/transformation of primary silicates into 2:1 clays and from incorporation of organic matter in the substrate (Lee et al. 2003; Bani et al. 2014), and subsequent uptake of Ni released by mineral dissolution.
- Formation of amorphous Fe-oxyhydroxides that have a CEC at high pH values (typically above 7–8, which is the usual pH of slightly weathered ultramafic soils), and to which Ni is easily reversibly sorbed (Chardot et al. 2007) after being released during weathering.

Under tropical conditions, the intense loss of Si during lateritization favours the formation of Fe-oxides (e.g. goethite) (Hseu et al. 2018; van der Ent et al. 2018a) that incorporates high concentrations of Ni during the phases of dehydration of Fe-hydroxides, despite a lower affinity of Ni to crystallized Fe-oxyhydroxides (Massoura et al. 2006). Further evolution of goethite can lead to an important loss of Ni (Dublet et al. 2015) and Ni contents in resulting hematite may decrease further to reach those of the bedrock. Nickel is known to be unavailable from wellcrystallised Fe-oxides (e.g. hematite) that occur in ferricrete (Zelano et al. 2016a; Quintela-Sabarís et al. 2018). In the saprolite layers of Geric Ferralsols, Ni that is progressively leached by lateritization and the maturation of Ni-bearing Fe-oxides is accumulated to high concentrations in phyllosilicates (serpentine, talc, smectite), which commonly represent the best Ni lateritic ore. The prime example is saprolitic smectite (Decarreau et al. 1987) found on the pyroxenite of Niquelândia (Brazil), where Ni concentration reaches >20 wt%. The Ni borne by saprolitic smectite is one of the most available sources of Ni in soils globally (Raous et al. 2013). Vertic Cambisols (Hypermagnesic) described on many serpentinite outcrops in the tropics, such as in Cuba, Borneo, and New Caledonia (Proctor 2003), also display very high Ni availability, for the same geochemical and mineralogical reasons (van der Ent et al. 2018a). Where natural erosion or mining has removed the lateritic horizons of ultramafic Ferralsols, the resulting soils have similar geochemical properties as the natural Vertic Cambisols (Hypermagnesic) found on serpentinite (Garnier et al. 2009b). Tropical Ni hyperaccumulators are generally native to these two types of environments (van der Ent et al. 2016a, 2018a). Geric Ferralsols having well-established ferricrete lack hyperaccumulator species owing to the absence of available Ni (Raous et al. 2010, 2013; Zelano et al. 2016a; van der Ent et al. 2016a).

Finally, vegetation and possibly Ni-hyperaccumulators are very active at recycling Ni in topsoil (Estrade et al. 2015; Ratié et al. 2019). As such, hyperaccumulator plants provide organic matter that increases the CEC and releases significant amounts of Ni through litter and the decay of organic matter. The result is a very mobile pool of Ni in the surface of soils (Bani et al. 2014). The role of biogeochemical recycling for maintaining sufficient levels of essential elements in acidic forest topsoils have been elucidated recently (Laclau et al. 2010); it is probable that the same processes control Ni geochemistry in ultramafic soils and ecosystems worldwide.

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